

Chapter 13

Quality Assessment and Statistical Analysis of Air Monitoring Data

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1.0 Introduction

On October 17, 2006, the USEPA amended its national air quality monitoring requirements. This rule changed a number of requirements in 40 CFR Part 58 Appendix A, the section which describes the planning, implementation, assessment and reporting of the ambient air monitoring quality system. One important change was the statistical techniques used to estimate the precision and bias of the various quality control and performance evaluation checks included in Appendix A. Prior to this revision, the statistics used to estimate precision and bias (then called accuracy) were developed in the late 1970's. In 1983, the guidance document titled "*Guideline on the Meaning and Use of Precision and Accuracy Data Required by 40 CFR Part 58 Appendices A and B*" (hereafter referred to as "1983 Guideline") was developed as a companion to Appendix A and B to help explain the rationale for the statistics and how they were used.

1.1 Air Quality System (AQS)

The Air Quality System is database administered by the U.S. Environmental Protection Agency (USEPA) used to assess the status of the Nation's air quality. The system includes a repository of ambient concentrations of air pollutants and associated meteorological data as well as software used to provide statistical analysis of this data. Precision and accuracy data which assess the quality of the air pollutant data is also contained in the AQS.

The Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section (IDEM, OAQ, QAS), must submit to the USEPA - AQS, within 90 days after the end of each quarter, the results of all required valid precision, bias, and accuracy tests conducted within the state during that quarter. This data is from monitoring networks operated by industries, consultants, local agencies, and IDEM. In order to meet the 90-day deadline, all precision, bias, and accuracy data from each reporting agency in Indiana must be submitted to the OAQ/QAS within 60 days after the end of each quarter.

1.2 Monitoring Quality Objectives (MQO)

The USEPA's Ambient Air Quality Monitoring Program is implemented under the authority of the Clean Air Act to provide air quality data for one or more of the three following objectives:

- Provide air pollution data to the general public in a timely manner.
- Support compliance with air quality standards and emissions strategy development.
- Support air pollution research studies.

In order to support the objectives the monitoring networks are designed with a variety of monitoring sites that generally fall into the following categories which are used to:

1. determine the highest concentrations expected to occur in the area covered by the network;
2. determine typical concentrations in areas of high population density;

3. determine the impact on ambient pollution levels of significant sources or source categories;
4. determine the general background concentration levels;
5. determine the extent of regional pollutant transport among populated areas, and in support of secondary standards; and
6. measure air pollution impacts on visibility, vegetation damage, or other welfare-based impacts.

These different objectives can potentially require information of varying quality. USEPA recognized the importance of collecting data of acceptable and consistent quality. In the late 1970's USEPA started developing consistent techniques to identify the objectives that required the highest quality data and then to develop a set of requirements to collect and assess this measurement quality information. The USEPA embarked on the process very similar to what is now called the Data Quality Objectives (DQO) Process and determined that the comparison of data to the National Ambient Air Quality Standards (NAAQS) was the highest priority objective and that data would be collected in a manner that minimized the uncertainty in making attainment decisions. The ambient air monitoring regulations were revised in 1979 and at that time two Appendices were added:

- Appendix A- Quality Assurance Requirements for State and Local Monitoring Stations (SLAMS)
- Appendix B-Quality Assurance Requirements for Prevention of Significant Deterioration (PSD) Monitoring

These appendices established the development of a quality assurance program to be implemented at the reporting organization level of aggregation. The appendices identified quality control, audits, and performance evaluation techniques that would be implemented internally as well as by external organizations like the USEPA Regions, ORD, and OAQPS, and established the statistical techniques to evaluate the data quality indicators. The primary data quality indicators for the ambient air program were identified as precision and accuracy (P&A). The 1983 Guideline provided a rationale for the use of the P&A data that was required to be collected in the two appendices mentioned. As was written in the 1983 Guideline, "the P&A statistics represented a compromise between (a) theoretical statistical exactness, and (b) simplicity and uniformity in computational procedures". The P&A statistics were aggregated by reporting organization over various time periods and combined into a probability limit estimate.

In 1998, with the promulgation of the PM_{2.5} NAAQA, USEPA formally implemented the DQO process and established acceptance criteria for precision and bias using statistics which were a departure from the statistics in the 1983 Guideline.

During this time period, OAQPS and the monitoring organizations were cooperating to develop a new Monitoring Strategy. OAQPS formed a QA Strategy Workgroup that set out to perform a thorough review of the Appendix A requirements and improve the quality system where appropriate.

One outcome of this review was the suggestion that USEPA look at a way to provide a more consistent set of statistics for the estimates of precision and bias. As part of this process, the Workgroup endorsed the use of the DQO process and the measurement quality objectives

1.3 Data Quality Objectives (DQO), Data Quality Indicators (DQI) & Measurement Quality Objectives (MQO)

In order to provide decision makers with data of acceptable quality, OAQPS uses the DQO process to determine the data quality requirements for the ambient air criteria pollutants. Data quality objectives (DQOs) are a full set of performance constraints needed to design an environmental data operation (EDO), including a specification of the level of uncertainty (error) that a decision maker (data user) is willing to accept in the data to which the decision will apply. Throughout this document, the term *decision maker* is used. This term represents individuals that are the ultimate users of ambient air data and therefore may be responsible for: setting the NAAQS, developing a quality system, evaluating the data, or comparing data to the NAAQS. The DQO will be based on the data requirements of the decision maker. Decision makers need to feel confident that the data used to make environmental decisions are of adequate quality. The data used in these decisions are never error free and always contain some level of uncertainty. Because of these uncertainties or errors, there is a possibility that decision makers may declare an area “nonattainment” when the area is actually in “attainment” or “attainment” when actually the area is in “nonattainment”. Figures 1 and 2 illustrate how errors can affect a NAAQS attainment/nonattainment decision based on an annual mean concentration value of 15. There are serious political, economic and health consequences of making such decision errors. Therefore decision makers need to understand and set limits on the probabilities of making incorrect decisions with these data.

In order to set probability limits on decision errors, one needs to understand and attempt to control uncertainty. Uncertainty is used as a generic term to describe the sum of all sources of error associated with an EDO. Uncertainty can be illustrated as follows:

$$S_o^2 = S_p^2 + S_m^2$$

Where:

S_o = overall uncertainty

S_p = population uncertainty (spatial and temporal)

S_m = measurement uncertainty (data collection)

The estimate of overall uncertainty is an important component in the DQO process. Both population and measurement uncertainties must be understood. The DQOs are assessed through the use of data quality indicators (DQIs) which are the quantitative statistics and the qualitative descriptors used to interpret the degree of acceptability or utility of data to the user. The DQIs can then be used to establish the MQOs. Once the MQOs are established and monitoring is implemented, data quality assessments (DQAs) are performed to determine whether the DQOs were achieved. If not, the monitoring program should take steps to identify the major sources of uncertainty and find ways to reduce these uncertainties to the acceptable levels.

1.3.1 Data Quality Indicators (DQI)

Data quality indicators are:

Representativeness – the degree in which data accurately and precisely represents a characteristic of a population, parameter variation at a sampling point, a process condition, or an environmental condition.

Precision – a measure of mutual agreement among individual measurements of the same property usually under prescribed conditions. This is the random component of error. Precision is estimated by various statistical techniques using some derivation of the standard deviation.

Bias – the systematic or persistent distortion of a measurement process which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

Detectability – the determination of the low range critical value of a characteristic that a method specific procedure can reliably discern.

Completeness – a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

Comparability – a measure of confidence with which one data set can be compared to another.

Accuracy has been a term frequently used to represent closeness to “truth” and includes a combination of precision and bias error components. This term had been used throughout the CFR but has been replaced with bias when there is the ability to distinguish precision from bias.

The quality system for the ambient air monitoring program focuses on understanding and controlling (as much as possible) measurement uncertainty and because of that, mainly focuses on the data quality indicators of precision, bias, detectability, completeness and comparability. Representativeness is addressed through network designs and is not, per-se, something that the quality system can control through better measurements.

1.3.2 Measurement Quality Objectives (MQO)

For each DQI one must identify a level of uncertainty or error that is acceptable and will achieve the DQO. MQOs are designed to evaluate and control various phases (sampling, preparation, analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the DQOs. This finally gets us to CFR where the various quality control checks, like the one-point quality control check for the gaseous pollutants or the particulate matter collocated instruments, are established. These checks help quantify a data quality indicator and their acceptance criteria are the MQOs. Table 1 provides a complete listing of the required measurement quality checks and the MQOs as they are currently defined in Appendix A.

USEPA has not changed the types of samples it uses to assess precision and bias. Although the 2006 rule has changed some of the names and some of their sampling frequencies, the basic checks are the same. Although the types of checks have not changed, USEPA changed the statistics used to evaluate precision and bias and in some cases how the measurement quality data are aggregated.

1.4 Primary Quality Assurance Organization (PQAO)

Monitoring data is collected and submitted to AQS by reporting organization. Precision, accuracy & bias data is submitted to AQS by Primary Quality Assurance Organization. A primary quality assurance organization is defined as a monitoring organization or a coordinated aggregation of such organizations that is responsible for a set of stations that monitors the same pollutant and for which data quality assessments can logically be pooled. Each criteria pollutant sampler/monitor at a monitoring station in the SLAMS network must be associated with one, and only one, primary quality assurance organization. Under the above definitions it is possible to have a PQAO with more than one reporting organization associated with it.

Each primary quality assurance organization shall be defined such that measurement uncertainty among all stations in the organization can be expected to be reasonably homogeneous, as a result of common factors. Common factors that should be considered by monitoring organizations in defining primary quality assurance organizations include:

- (a) Operation by a common team of field operators according to a common set of procedures;
- (b) Use of a common QAPP or standard operating procedures;
- (c) Common calibration facilities and standards;
- (d) Oversight by a common quality assurance organization; and
- (e) Support by a common management, laboratory or headquarters.

Primary quality assurance organizations are not necessarily related to the organization reporting data to the AQS.

1.5 New Statistics

As the result of review a revision was made in the precision and bias statistics. Confidence intervals will be used as a means for determining whether the bias and precision variables meet the measurement quality objectives. Confidence intervals allow organizations that show tight acceptable results the flexibility in reducing the frequency of certain QC checks. For example, the site with a bias of 5% plus or minus 1% likely does not need as many QC checks as the site with the bias of 5% plus or minus 10%. The acceptance criteria are based on the number of years of data that coincide with the time frame of the ambient air quality standards. For example, since the 8-hour ozone standard is based on three years of data, the acceptance criteria for bias and precision will also be based on three years of data.

Additionally, the acceptance criteria apply to each site operating an automated method.

For the automated methods, estimates of both bias and precision are derived from the one-point quality control checks and then double-checked with the annual performance evaluations, independent State audits, and the NPAP Program. To test the reasonableness of estimating bias and precision from bi-weekly checks, the FW (Focus Workgroup) made up some actual/indicated data pairs, assuming different levels of bias and precision, and tested a couple of proposed statistics. The FW simulated three years of data and provided summary statistics at the quarterly, annual, and 3-year level. For each scenario, the data was summarized by the three methods below:

1. **CFR Probability Interval.** For these statistics, USEPA reviewed what was currently in CFR, namely the overall percent difference in the actual and indicated concentrations and an associated probability interval that shows where 95% of all the percent differences should fall. Note that this does not provide separate estimates of bias and precision.
2. **Signed Bias & Precision (CV).** For this case, USEPA estimate bias and precision separately and also estimated confidence intervals for bias and confidence intervals for precision. A comment on this approach is that if there is trend in bias, such as +10% one year, 0% the next year, and -10% the third year, then, from a 3-year perspective, you may say the system is unbiased but very variable. This is how these statistics treat the trend in bias. Thus the bias tends to be small and the precision large, in general.
3. **Absolute Bias & Precision (CV).** As with the signed case above, USEPA estimated bias and precision separately and also estimated confidence intervals for bias and confidence intervals for precision. However, since the absolute value for bias is used, if there is trend in bias, such as +10% one year, 0% the next year, and -10% the third year, then, from a 3-year perspective, one may say the system has a great potential for bias but is precise. This is how these statistics treat the trend in bias. Thus the bias tends to be large and the precision small, in general.

2.0 National Performance Evaluation and Technical Systems Audit

The Indiana Department of Environmental Management, Office of Air Quality participates in USEPA's National Performance Audit Program (NPAP) and the PM Performance Evaluation Program (PEP) program. Technical systems audits by USEPA Region 5 are conducted at least every three years and results are reported to the AQS.

3.0 Ambient Data Submission

Ambient data must be submitted to the IDEM Ambient Monitoring Section within 60 days after the end of the quarter. This will allow sufficient time for review before the AQS submittal deadline of 90 days after the end of each reporting calendar quarter. All ambient and precision and accuracy data submittals to AQS are done electronically via the internet.

4.0 Gaseous Precision and Bias Assessments

4.1 One-Point Quality Control Check for SO₂, NO₂, O₃, and CO

Manual one-point quality control (QC) check is performed once every week on each analyzer used to measure SO₂, NO₂, O₃, and CO. The frequency of QC checks was increased from the minimum of once every two weeks because Indiana Department of Environmental Management (IDEM) has automated all of its air monitoring stations with automated calibration systems. The QC check is made by challenging the analyzer with a QC check gas of known concentration between 0.01 and 0.10 parts per million (ppm) for SO₂, NO₂, and O₃, and between 1 and 10 ppm for CO analyzers. The ranges allow for appropriate check gas selection for sites that may be sampling for different objectives, i.e., NCORE trace gas monitoring versus comparison to National Ambient Air Quality Standards (NAAQS).

4.1.1 Single Analyzer Precision

All precision checks start with a comparison of an audit concentration to the concentration measured by the analyzer and use percent difference as the comparison statistic as described in Equation 1. For each single point precision audit, calculate the percent difference, d_i as follows:

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Where, meas is the concentration indicated by the monitoring organization's analyzer and audit is the audit concentration of the standard used in the precision (QC) check being measured.

4.1.2 Precision Estimate

The precision estimate is used to assess the one-point precision (QC) checks for SO₂, NO₂, O₃, or CO described in Section 2.1 of this chapter. The precision estimator is the coefficient of variation upper bound and is calculated using Equation 2.

Equation 2:

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} d_i^2 - \left(\sum_{i=1}^n d_i \right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X_{0.1, n-1}^2}}$$

Where, $X_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with n-1 degrees of freedom.

4.2 Bias

The bias estimate is calculated using the one-point precision (QC) checks for SO₂, NO₂, O₃, or CO described in Section 2.1 of this chapter. The bias estimator is an upper bound on the mean absolute value of the percent differences as described in Equation 3:

Equation 3:

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where, n is the number of single point checks being aggregated; $t_{0.95, n-1}$ is the 95th quartile of a t-distribution with n-1 degrees of freedom; the quantity AB is the mean absolute values of the d_i 's and is calculated using Equation 4:

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the d_i 's and is calculated using Equation 5:

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculate in Equation 3 uses absolute values, it does not have a tendency (negative or positive bias) associated with it. A sign will be designated by rank ordering the percent differences of the precision (QC) check samples from a given site for a particular assessment interval. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs.

The annual performance evaluations for SO₂, NO₂, O₃, or CO are used to verify the results obtained from the one-point QC checks and to validate those results across a range of concentration levels. To quantify this annually at the site level and at the 3-year primary quality assurance organization level, probability limits will be calculated from the one-point QC checks using Equations 6 and 7:

Equation 6:

$$\text{Upper Probability Limit} = m + 1.96 \cdot S$$

Equation 7:

$$\text{Lower Probability Limit} = m - 1.96 \cdot S$$

Where, m is the mean (Equation 8)

Equation 8:

$$m = \frac{1}{k} \cdot \sum_{i=1}^k d_i$$

Where, k is the total number of one point QC checks for the interval being evaluated and S is the standard deviation of the percent differences (Equation 9 of this chapter) as follows:

Equation 9:

$$S = \sqrt{\frac{k \cdot \sum_{i=1}^k d_i^2 - \left(\sum_{i=1}^k d_i \right)^2}{k(k-1)}}$$

Percent differences for the performance evaluations, calculated using Equation 1 of this chapter can be compared to the probability intervals for the respective site or at the primary quality assurance organization level. Ninety-five percent of the individual percent differences (all audit concentration levels) for the performance evaluations should be captured within the probability intervals for the primary quality assurance organization.

5.0 Precision Estimates from Collocated Samples

At low concentrations, agreement between the measurements of collocated samplers, expressed as relative percent difference or percent difference, may be relatively poor. For this reason, collocated measurement pairs are selected for use in the precision calculations only when both reporting and duplicate sampler measurements are above the concentrations listed in Table 1.

Table 1
Minimum Concentration Levels for
Particulate Matter Precision Assessments

Parameter	Limit ($\mu\text{g}/\text{m}^3$)
PM _{2.5}	3
PM _{10-2.5}	3
PM ₁₀ (Lo-Vol)	3
PM ₁₀ (Hi-Vol)	15
Pb	0.02

The QAS recommends all reporting agencies calculate parameter precision, bias, accuracy, and perform other statistical analysis on a continuing basis. Calculate upgraded statistics after each

audit for each analyzer/pollutant, and for PM₁₀, PM_{2.5}, and Pb, as soon as analytical results become available.

Precision is aggregated at the primary quality assurance organization (PQAO) level quarterly, annually, and at the 3-year level. For each collocated data pair, the relative percent difference, d_i , is calculated by Equation 10.

Equation 10:

$$d_i = \frac{y_i - x_i}{\frac{1}{2}(y_i + x_i)}$$

Where x_i is the concentration of the primary sampler and y_i is the concentration value from the audit sampler. The precision upper bound statistic, CV_{ub} is a standard deviation on d_i with a 90 percent upper confidence limit (Equation 11).

Equation 11:

$$CV_{ub} = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} d_i^2 - \left(\sum_{i=1}^n d_i \right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{X_{0.1, n-1}^2}}$$

Where, n is the number of valid data pairs being aggregated, and $X_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with $n-1$ degrees of freedom. The factor of 2 in the denominator adjusts for the fact that each d_i is calculated from two values with error.

6.0 PM_{2.5} Bias Assessment

The bias estimate is calculated using the Performance Evaluation Program (PEP) audits described in CFR, section 4.1.3 of Part 58, Appendix A. The bias estimator is based on upper and lower probability limits on the mean percent differences (Equation 1). The mean percent difference, D , is calculated by Equation 12 below.

Equation 12:

$$D = \frac{1}{n_j} \cdot \sum_{i=1}^{n_j} d_i$$

Confidence intervals can be constructed for these average bias estimates in Equation 12 of this document using Equations 13 and 14:

Equation 13:

$$\text{Upper 90\% Confidence Interval} = D + t_{0.95,df} * \frac{s_d}{\sqrt{n_j}}$$

Equation 14:

$$\text{Lower 90\% Confidence Interval} = D - t_{0.95,df} * \frac{s_d}{\sqrt{n_j}}$$

Where, $t_{0.95,df}$ is the 95th quantile of a t-distribution with degrees of freedom $df = n_j - 1$ and s_d is an estimate of the variability of the average bias and is calculated using Equation 15 below:

Equation 15:

$$s_d = \sqrt{\frac{\sum_{i=1}^{n_j} (d_i - D)^2}{(n_j - 1)}}$$

7.0 PM_{10-2.5} and PM_{2.5} Absolute Bias Assessment

The bias estimate is calculated using the Performance Evaluation Program (PEP) audits described in CFR, section 4.1.3 of Part 58, Appendix A. The bias estimator is an upper bound on the mean absolute value of the percent differences (Equation 1), as described in Equation 3 as follows:

Equation 3:

$$|bias| = AB + t_{0.95,n-1} * \frac{AS}{\sqrt{n}}$$

Where n is the number of PEP audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i 's (calculated by Equation 1) and is expressed as Equation 4 as follows:

Equation 4:

$$AB = \frac{1}{n} * \sum_{i=1}^n |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the d_i 's (Equation 1) and is calculated using Equation 5 as follows:

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculated in Equations 3 and 6 of this chapter uses absolute values, it does not have a sign direction (negative or positive bias) associated with it. A sign will be designated by rank ordering the percent differences of the QC check samples from a given site for a particular assessment interval. Calculate the 25th and 75th percentiles of the percent differences for each site. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs (i.e. straddling zero).

8.0 One-Point Flow Bias Estimate

The bias estimate is calculated using the collocated audits previously described. The bias estimator is an upper bound on the mean absolute value of the percent differences (Equation 1), as described in Equation 3 as follows:

Equation 3:

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where n is the number of flow audits being aggregated; $t_{0.95, n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i 's (calculated by Equation 1) and is expressed as Equation 4 as follows:

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the d_i 's (Equation 1) and is calculated using Equation 5 as follows:

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculated in Equations 3 of this chapter uses absolute values, it does

not have a sign direction (negative or positive bias) associated with it. A sign will be designated by rank ordering the percent differences of the QC check samples from a given site for a particular assessment interval. Calculate the 25th and 75th percentiles of the percent differences for each site. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs (i.e. straddling zero).

9.0 Semi-Annual Flow Rate Audits

Flow rate audits are required to be performed on a semi-annual frequency spaced no closer than three months apart and no more than 9 months apart. The Indiana Department of Environmental Management performs flow rate audits each calendar quarter (4 per year) using the same spacing criteria.

The flow rate audits are used to assess the results obtained from the one-point flow rate verifications and to provide an estimate of flow rate acceptability. For each flow rate audit, calculate the percent difference in volume using Equation 1 of this document where *meas* is the value indicated by the sampler's volume measurement and *audit* is the actual volume indicated by the auditing flow meter.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

To quantify this annually at the site level and at the 3-year primary quality assurance organization level, probability limits are calculated from the percent differences using Equations 6 and 7 of this document where *m* is the mean described in Equation 8 of this document and *k* is the total number of one-point flow rate verifications for the year

Equation 6:

$$\text{Upper Probability Limit} = m + 1.96 \cdot S$$

Equation 7:

$$\text{Lower Probability Limit} = m - 1.96 \cdot S$$

Where, *m* is the mean (Equation 8)

Equation 8:

$$m = \frac{1}{k} \cdot \sum_{i=1}^k d_i$$

Where, *k* is the total number of one point QC checks for the interval being evaluated and *S* is the standard deviation of the percent differences (Equation 9 of this chapter) as follows:

Equation 9:

$$S = \sqrt{\frac{k \cdot \sum_{i=1}^{k_i} d_i^2 - \left(\sum_{i=1}^k d_i \right)^2}{k(k-1)}}$$

10.0 Lead Bias Assessments

10.1 Test Procedures for Methods for Lead

10.1.1 Sample Collection

Collect simultaneous 24-hour samples (filters) of lead at the test site or sites using proper reference methods until at least 10 filter pairs have been obtained. If the conditions of 40 CFR Part 53.30 (d) (4) apply, collect at least 10 common samples (filters) in accordance with 40 CFR Part 53.30 (d) (4) and divide each to form the filter pairs.

10.1.2 Audit Samples

Six audit samples, comprised of three strips at each of two different concentration ranges, are required to be analyzed each quarter. The audit samples are ¾ X 8 inch glass fiber strips. The lower concentration range is 30-100% of the NAAQS and the higher concentration is 200-300% of the NAAQS.

10.1.3 Filter Analysis

For each audit sample, analyze each filter extract three times in accordance with the reference method analytical procedure. The analysis of replicates should not be performed sequentially, i.e., a single sample should not be analyzed three times in sequence. Calculate the indicated lead concentrations for the reference method samples in µg/m³ for each analysis of each filter.

Calculate the indicated total lead amount for the audit samples in µg/strip for each analysis of each strip. Label these test results as R_{1A}, R_{1B}, R_{1C}, R_{2A}, R_{2B}, ..., Q_{1A}, Q_{1B}, Q_{1C}, ..., where R denotes results from the reference method samples; Q denotes results from the audit samples; 1, 2, 3 indicate the filter number, and A, B, C indicate the first, second, and third analysis of each filter, respectively.

10.1.4 Average Lead Concentration

Calculate average lead concentrations for each filter by averaging the concentrations calculated from the three analyses.

10.1.5 Lead Strips

Each calendar quarter audit the Pb Reference Method analytical procedure using glass fiber filter strips containing a known quantity of Pb. These audit sample strips are prepared by depositing a

Pb solution on unexposed glass fiber filter strips of dimensions 1.9 centimeters (cm) by 20.3 cm (3/4 inch by 8 inch) and allowing them to dry thoroughly. The audit samples must be prepared using batches of reagents different from those used to calibrate the Pb analytical equipment being audited. Prepare audit samples in the following concentration ranges:

Range	Pb concentration $\mu\text{g}/\text{strip}$	(Equivalent ambient Pb concentration, $\mu\text{g}/\text{m}^3$) ¹
1	9-30	.045-0.15
2	60-90	0.3-0.45

¹ Equivalent ambient Pb concentration in $\mu\text{g}/\text{m}^3$ is based on sampling at 1.7 m^3/min for 24 hours on a 20.3 cm x 25.4 cm (8 inch x 10 inch) glass fiber filter.

- (a) Audit samples must be extracted using the same extraction procedure used for exposed filters.
- (b) Analyze three audit samples in each of the two ranges each quarter samples are analyzed. The audit sample analyses shall be distributed as much as possible over the entire calendar quarter.
- (c) Report the audit concentrations (in μg Pb/strip) and the corresponding measured concentrations (in μg Pb/strip) using AQS unit code 077. The relative percent differences between the concentrations are used to calculate analytical accuracy as described in this chapter.
- (d) The audits of an equivalent Pb method are conducted and assessed in the same manner as for the reference method. The flow auditing device and Pb analysis audit samples must be compatible with the specific requirements of the equivalent method.

In order to estimate bias, the information from the flow rate audits and the Pb strip audits should be combined as described below. To be consistent with the formulas for the gases, the recommended procedures are to work with relative errors of the lead measurements. The relative error in the concentration is related to the relative error in the volume and the relative error in the mass measurements using Equation 16 of this chapter:

Equation 16:

$$rel.error = \frac{(measured\ concentration - audit\ concentration)}{audit\ concentration}$$

$$rel.error = \left(\frac{1}{1 + rel.error} \right) (rel.mass\ error - rel.volume\ error)$$

As with the gases, an upper bound for the absolute bias is desired. Using Equation 16 above, the absolute value of the relative (concentration) error is bounded by Equation 17 of this chapter:

Equation 17:

$$|rel.error| \leq \frac{|relative\ mass\ error| + |relative\ volume\ error|}{1 - |relative\ volume\ error|}$$

The quality indicator data collected are then used to bound each part of Equation 17 separately.

“Flow Audit” calculations

For each flow rate audit, calculate the percent difference, d_i , in volume by Equation 1 where *meas* is the value indicated by the sampler’s volume measurement and *audit* is the actual volume indicated by the auditing flow meter.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

The absolute “volume bias” upper bound is then calculated using Equation 3 of this chapter where n is the number of flow rate audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i ’s and is calculated using Equation 4, and the quantity AS in Equation 3 of this chapter is the standard deviation of the absolute values of the d_i ’s and is calculated using Equation 5 of this chapter.

Equation 3:

$$|bias| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where n is the number of flow audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i ’s (calculated by Equation 1) and is expressed as Equation 4 as follows:

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the d_i ’s (Equation 1) and is calculated using Equation 5 as follows:

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

“Pb Strip Audit” calculations

Similarly for each lead strip audit, calculate the percent difference, d_i in mass by Equation 1 where *meas* is the value indicated by the mass measurement and *audit* is the actual lead mass on the audit strip.

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

The absolute “mass bias” upper bound is then calculated using Equation 3 of this chapter where n is the number of lead strips audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom;

Equation 3:

$$|bias| = AB + t_{0.95,n-1} \cdot \frac{AS}{\sqrt{n}}$$

Where n is the number of flow audits being aggregated; $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom; the quantity AB is the mean of the absolute values of the d_i 's (calculated by Equation 1) and is expressed as Equation 4 as follows:

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity AS is the standard deviation of the absolute value of the d_i 's (Equation 1) and is calculated using Equation 5 as follows:

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Final |Bias| calculation

Finally, the absolute bias upper bound is given by combining the absolute bias estimates of the flow rate and Pb strips using Equation 18 of this chapter:

Equation 18:

$$|bias| \leq \frac{|mass\ bias| + |vol.\ bias|}{100 - |vol.\ bias|}$$

Where mass bias is the bias calculated for the Pb strips, and vol is the bias calculated for the flow rate audits.

Since the bias statistic as calculated in Equation 3 of this document uses absolute values, it does not have a sign direction (negative or positive bias) associated with it. A sign will be designated by rank ordering the percent differences of the QC check samples from a given site for a particular assessment interval. Calculate the 25th and 75th percentiles of the percent differences for each site. The absolute bias upper bound should be flagged as positive if both percentiles are positive and negative if both percentiles are negative. The absolute bias upper bound would not be flagged if the 25th and 75th percentiles are of different signs (i.e. straddling zero).

Time Period for Audits

The statistics in this section assume that the mass and flow rate audits represent the same time period. Since the two types of audits are not performed at the same time, the audits need to be grouped by common time periods. Consequently, the absolute bias estimates should be done on annual and 3-year levels. The flow rate audits are site-specific, so the absolute bias upper bound estimate can be done and treated as a site-level statistic.

11.0 Accuracy

Estimates of the accuracy of automated methods are calculated from the results of independent audits (See Chapter 1 for accuracy audit procedures). Although not required by the USEPA, the QAS recommends that all reporting agencies perform accuracy audits not less than once each quarter for each analyzer. More frequent accuracy audits are encouraged to help troubleshoot any problems and to see how linear the analyzer is over the whole sampling range. The audit device used for the accuracy audit must be different from the device used to calibrate the analyzer.

A November 10, 2010, memo from OAQPS expanded the accuracy audit levels from five to ten. The new accuracy audit levels incorporate trace level CORE analyzer ranges along with the traditional ambient level analyzer ranges and are specific to the continuous measurements of:

- SO₂ – Sulfur Dioxide
- CO – Carbon Monoxide
- NO₂ – Nitrogen Dioxide
- O₃ – Ozone

Table 2
Accuracy Audit Concentration Levels

Audit Level	Concentration Range (ppm)							
	O ₃		SO ₂		NO ₂		CO	
	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
1	0.0040	0.0059	0.0003	0.0029	0.0003	0.0029	0.020	0.059
2	0.0060	0.0190	0.0030	0.0049	0.0030	0.0049	0.600	0.199
3	0.0200	0.0390	0.0050	0.0079	0.0050	0.0079	0.200	0.899
4	0.0400	0.0690	0.0080	0.0199	0.0080	0.0199	0.900	2.999
5	0.0700	0.0890	0.0200	0.0499	0.0200	0.0499	3.000	7.999
6	0.0900	0.1190	0.0500	0.0999	0.0500	0.0999	8.000	15.999
7	0.1200	0.1390	0.1000	0.1499	0.1000	0.2999	16.000	30.999
8	0.1400	0.1690	0.1500	0.2599	0.3000	0.4999	31.000	39.999
9	0.1700	0.1890	0.2600	0.7999	0.5000	0.7999	40.000	50.000
10	0.1900	0.2590	0.8000	1.0000	0.8000	1.0000	50.000	60.000

11.1 Single Analyzer Accuracy

Accuracy formulas and calculations remain the same and are presented in the following sections.

Calculate the percent difference (d_i) for each audit concentration level using Equation 1.

Note: The correct concentration levels for accuracy audits are listed above in Table 2.

11.2 Accuracy for Primary Quality Assurance Organization

Using Equation 8, calculate for each audit concentration level the average (D) (Equation 12) of the individual percent differences (d_i) for all analyzers (n) measuring a given pollutant.

Using Equation 9, calculate for each audit concentration level the standard deviation (S) of all the different percent differences for all analyzers audited. Repeat this for each pollutant.

For each pollutant, calculate the 95 percent probability limits for the accuracy of the reporting organization at each concentration level using Equations 6 and 7.

12.0 PAMS Volatile Organic Compounds (VOC)

Consult Chapter 8 of the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Manual for details on precision and accuracy requirements.

13.0 Submittal of Precision and Accuracy Data

The precision and accuracy reports should be submitted to the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section. This information will be reviewed and submitted to USEPA's AQS system.

APPENDIX A - EQUATIONS

Equation 1:

$$d_i = \frac{meas - audit}{audit} \times 100$$

Equation 2:

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} d_i^2 - \left(\sum_{i=1}^n d_i \right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X_{0.1, n-1}^2}}$$

Equation 3:

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

Equation 4:

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

Equation 5:

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} |d_i|^2 - \left(\sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Equation 6:

$$\text{Upper Probability Limit} = m + 1.96 \cdot S$$

Equation 7:

$$\text{Lower Probability Limit} = m - 1.96 \cdot S$$

Equation 8:

$$m = \frac{1}{k} \cdot \sum_{i=1}^k d_i$$

Equation 9:

$$S = \sqrt{\frac{k \cdot \sum_{i=1}^{k_j} d_i^2 - \left(\sum_{i=1}^k d_i \right)^2}{k(k-1)}}$$

Equation 10:

$$d_i = \frac{y_i - x_i}{\frac{1}{2}(y_i + x_i)}$$

Equation 11:

$$CV_{ub} = \sqrt{\frac{n \cdot \sum_{i=1}^{n_j} d_i^2 - \left(\sum_{i=1}^n d_i \right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{X_{0.1, n-1}^2}}$$

Equation 12:

$$D = \frac{1}{n_j} \cdot \sum_{i=1}^{n_j} d_i$$

Equation 13:

$$\text{Upper 90\% Confidence Interval} = D + t_{0.95, df} * \frac{S_d}{\sqrt{n_j}}$$

Equation 14:

$$\text{Lower 90\% Confidence Interval} = D - t_{0.95, df} * \frac{S_d}{\sqrt{n_j}}$$

Equation 15:

$$s_d = \sqrt{\frac{\sum_{i=1}^{n_j} (d_i - D)^2}{(n_j - 1)}}$$